

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MORPETH, Fraser, Forrest
Avecia Limited
Intellectual Property Group
PO Box 42
Blackley, Manchester M9 8ZS
GRANDE BRETAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(PCT Rule 71.1)

<p>Applicant's or agent's file reference SMC 60606/WO</p>		<p>Date of mailing (day/month/year) 16.12.2005</p>	
International application No. PCT/GB2004/002855	International filing date (day/month/year) 02.07.2004	Priority date (day/month/year) 18.07.2003	
<p>Applicant AVECIA INKJET LIMITED et al</p>			

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/B/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability requirements for enabling disclosure, clarity and support for the claims.

ENTERED INTO	DATE / INITIALS
20/12/05 GS	
REINDEER CREATED	
ATTORNEY	

<p>Name and mailing address of the international preliminary examining authority:</p> <p> European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016</p>	<p>Authorized Official TO BE VERIFIED ROSSIANA JCF Tel. +31 70 340-3322</p>
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PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60606/WO	FOR FURTHER ACTION		See Form PCT/IPEA/416
International application No. PCT/GB2004/002855	International filing date (<i>day/month/year</i>) 02.07.2004	Priority date (<i>day/month/year</i>) 18.07.2003	
International Patent Classification (IPC) or national classification and IPC C09B47/06, C09B47/26, C09B67/22, C09D11/00			
Applicant AVECIA INKJET LIMITED et al			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 12 sheets, as follows: <ul style="list-style-type: none"> <input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input checked="" type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. <input type="checkbox"/> <i>(sent to the International Bureau only)</i> a total of (indicate type and number of electronic carrier(s)), containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions). 			
<p>4. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input checked="" type="checkbox"/> Box No. VI Certain documents cited <input checked="" type="checkbox"/> Box No. VII Certain defects in the international application <input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application 			
Date of submission of the demand 21.02.2005	Date of completion of this report 16.12.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Ketterer, M Telephone No. +31 70 340-3645		

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/GB2004/002855

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
 - international search (under Rules 12.3 and 23.1(b))
 - publication of the international application (under Rule 12.4)
 - international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

Description, Pages

1-15, 17-22	as originally filed
16	received on 18.03.2005 with letter of 16.03.2005

Claims, Numbers

1-40	received on 18.03.2005 with letter of 16.03.2005
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a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. The amendments have resulted in the cancellation of:

- the description, pages
- the claims, Nos.
- the drawings, sheets/figs
- the sequence listing (*specify*):
- any table(s) related to sequence listing (*specify*):

4. This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- the description, pages
- the claims, Nos. 4-24,29-40
- the drawings, sheets/figs
- the sequence listing (*specify*):
- any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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International application No.
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-4,25-36
	No:	Claims	1,5-24,37-40
Inventive step (IS)	Yes:	Claims	2-4,25-36
	No:	Claims	1,5-24,37-40

Industrial applicability (IA)

Yes:	Claims	1-40
No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VI Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/GB2004/002855

Reference is made to the following documents:

- D1: EP -A- 1 239 010
- D2: US -A- 2001/0011396
- D3: WO -A- 01/66647
- D4: WO -A- 01/66648
- D5: WO -A- 03/068866
- D6: WO -A- 98/49239
- D7: WO -A- 2004/035701
- D8: WO -A- 2004/035700
- D9: WO -A- 03/089532

I.1. Amendments:

I.1.1. New Claim 4 is not allowable with respect to Article 19(2) PCT; the preferred combination of R1,R2 being H or optional C1-4 alkyl, R3 is H or methyl,R4 is opt. substituted hydrocarbyl ; or R3 and R4 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system; is not disclosed as such in one of the preferred embodiments. Therefore, all claims depending or referring back to this claim 4 violate Article 19(2) PCT as well.

I.1.2. Also claim 13 seems not to be allowable, because the condition R1,R2 being both H is connected to further conditions as set out on page 3, line 26 to page 4, line 14 in the preferred embodiments.

I.1.3. Furthermore, the specific combinations of the new claims 14,15,16 are not disclosed in the application as filed: first, all examples deal with Cu as metal; the claims 14-16 refer also back to claims dealing with Ni (see current claim 5); some examples deal with specific x,y,z-numbers; claims 14-16 refer back to claims with broader x,y,z-ranges. It is not allowed to generalise examples by taking specific features out of them and introduce them into generalised claims. All claims depending or referring back to claims 13-16 are not allowable as well.

I.1.4. New claim 29 is not allowable (please read item 1.2.).

I.1.5. New claims 30,31,32 are not allowable (please read item 1.3.).

V.1. Novelty:

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V.1.1. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1,5-24,37-40 is not new in the sense of Article 33(2) PCT.

The term 'major' used in current claim1 seems not to be sufficient to delimit the scope of claim 1 clearly from the disclosed prior art; as it is not clear in general, that the alpha resp. alpha/beta fraction comprised in the dye compositions of the prior art documents is the major fraction, they could implicitly disclose novelty destroying subject matter for current claim 1. Regarding the additional condition that the dyes are prepared resp. obtainable by starting from specific educts defines the scope of the subject matter intended to be claimed more clearly. Furthermore, reading pages 2,3 of the description and the examples 1 (stage 1) and 2 (stage 1 [similar to stage 1 in example 1]), the applicant starts exclusively from the pre-substituted starting components (appropriate 'beta'-sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide); therefore, current claims 2-4 as well as claims 26-28 can be regarded as being sufficiently disclosed in the sense of Article 5 PCT resp. sufficiently supported by the description in the sense of Article 6 PCT.

Therefore, all claims which do not contain the limiting process features concerning the specific educts, or all claims, which depend or refer back to such claims are still regarded being not novel over e.g. D9; these are the claims 1,5-24,37-40.

V.1.2. Claims 2-4,25-36 seem to be novel over the disclosed prior art.

The documents D1-D9 do not disclose dyestuff mixtures obtainable by a process as defined in claims 2-4 and 26-28.

V.2. Inventive step:

V.2.1. Claims 2-4,25-36 seem to involve an inventive step in the sense of Article 33(3) PCT.

Documents D5,D7,D8 are published after the international filing date of the current application. The claimed priority document related to this application supports the relevant parts of it. For the assessment of inventive step D5,D7,D8 are put aside, the documents D1-D4,D6,D9 are considered to be relevant.

The problem underlying the current application can be seen in 'providing ink jet inks bearing certain fastness properties, especially less fading on exposure to light or common oxidising gases such as ozone'.

Only D3,D4 deal with the problem of stability against ozone attacks and emphasised the improved fastness of the dyestuffs resp. inks prepared therein.

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This problem is, on the other hand, not related in D3,D4 to the substitution pattern of the dyes (alpha or beta positions) in discussion. In the current application it could be demonstrated that the claimed dyes, compared to a alpha/beta-substituted dye (comparative dye 2 resp. comparative ink 2), give a significant improvement concerning the ozone fastness.

The dyes disclosed in D3,D4 are of bichromophoric nature and do not come as close to the dyes of claims 2-4,25-36 as the comparative dye 2 mentioned in the application. An inventive step can therefore be accepted with respect to the dye compositions and mixtures of current claims 2-4,25-36.

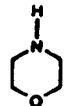
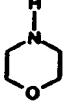
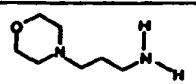
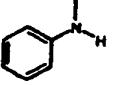
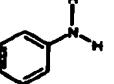
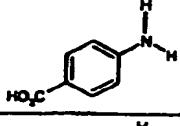
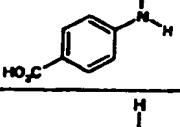
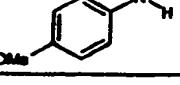
VI. Documents D5,D7,D8 are published after the international filing date of the current application. In case of entering the regional phase they probably could be of relevance with regard to Article 54(3)(4) EPC.

VII. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D3-D5,D7-D9 is not mentioned in the description, nor are these documents identified therein.

VIII. Article 5 PCT:

Concerning the disclosure of the current application, only dye mixtures are described produced by a process in which appropriate sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide compounds in the presence of a suitable reaction partners are used. This technical feature is missing in current claim 25. Claim 25 therefore does not comply with Article 5 PCT.

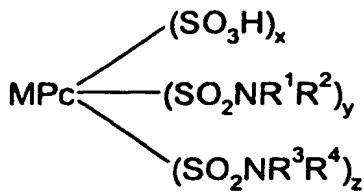
Table 1

Example	Amine R	Mol. Eq.Amine	Mol. Eq. Ammonia	Product		
				x	y	z
Example 3		3.3	0.5	0.5	2av	2av
Example 4		2.2	1.1	0.4	1.9av	1.9av
Example 6		2.2	1.1	0.9	1.7av	1.7av
Example 7	H ₂ NCH ₂ CH ₂ SO ₃ H	3.3	0.5	0.7	0.4	2.7
Example 8	H ₂ NCH ₂ CH ₂ SO ₃ H	2.2	1.1	0.5	0.9	2
Example 9	H ₂ NCH ₂ CH ₂ CO ₂ H	3.3	0.5	2.4	0.7	1.5
Example 10	H ₂ NCH ₂ CH ₂ CO ₂ H	2.2	1.1	2.3	1.1	0.9
Example 11	HN(CH ₃)CH ₂ CH ₂ SO ₃ H	2.2	1.1	1.3	0.9	1.8
Example 12	HN(CH ₃)CH ₂ CH ₂ SO ₃ H	3.3	0.5	1.4	0.7	2.4
Example 13	H ₂ NCH ₂ PO ₃ H ₂	2.2	1.1	1.2	0.3	2.7
Example 14	NH(CH ₂ CH ₂ SO ₃ H)(CH ₂ C H ₂ CONH ₂)	3.3	0.5	1.4	0.8	1.5
Example 15	NH(CH ₂ CH ₂ SO ₃ H)(CH ₂ C H ₂ CONH ₂)	2.2	1.1	1.2	1.0	1.3
Example 16		3	0.5	0.1	2av	2av
Example 17		2	1	0.5	1.8av	1.8av
Example 18		2	1.1	1.3	0.7av	0.7av
Example 19		3	0.5	1.3	0.7av	0.7av
Example 20		2	1.1	1	1.5av	1.5av

CLAIMS

1. A composition comprising:

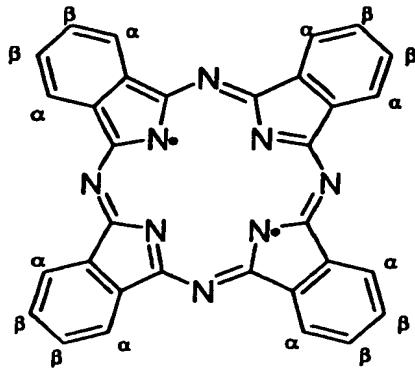
(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;
Pc represents a phthalocyanine nucleus of formula;



R¹ and R² independently are H or optionally substituted C₁₋₄alkyl;

R³ is H or optionally substituted hydrocarbyl; and

R⁴ is optionally substituted hydrocarbyl; or

R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

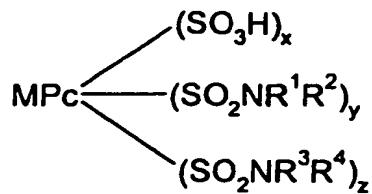
the sum of $(x+y+z)$ is 4; and

the substituents, represented by x, y and z, are attached only to a β -position on the phthalocyanine ring; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

2. A composition according to claim 1 comprising:

(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:

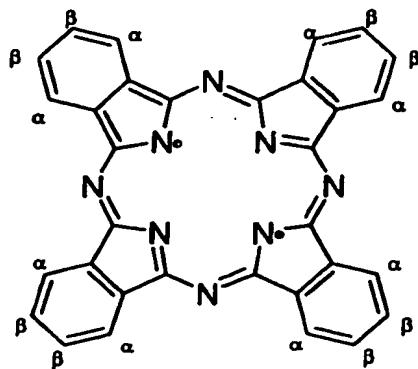


Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



R^1 and R^2 independently are H or optionally substituted C_{1-4} alkyl;

R^3 is H or optionally substituted hydrocarbyl; and

R^4 is optionally substituted hydrocarbyl; or

R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

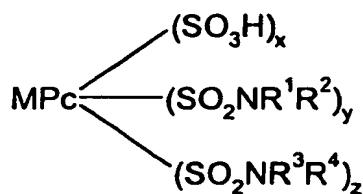
the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by a process which comprises cyclisation of appropriate β -sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base followed by chlorination and then amination/amidation; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

3. A composition according to either claim 1 or claim 2 comprising:

(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:

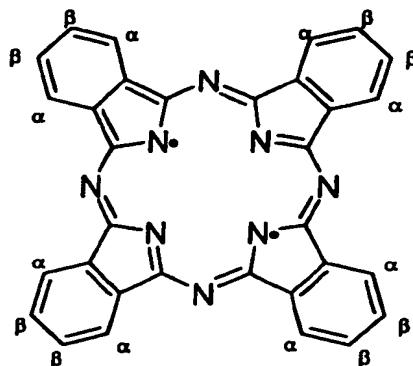


Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



R^1 and R^2 independently are H or optionally substituted C_{1-4} alkyl;

R^3 is H or optionally substituted hydrocarbyl; and

R^4 is optionally substituted hydrocarbyl; or

R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

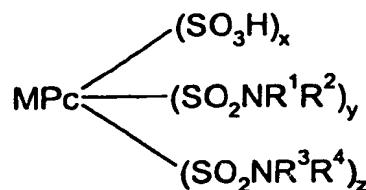
the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by cyclisation of 4-sulfo-phthalic acid in the presence of a nitrogen source a copper or nickel salt and a base to give phthalocyanine β -tetrasulfonic acid which is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula HNR^1R^2 and HNR^3R^4 wherein R^1 , R^2 , R^3 and R^4 are as hereinbefore defined; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

4. A composition according to claim 1 comprising:

(a) a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

R¹ and R² independently are H or optionally substituted C₁₋₄alkyl;

R³ is H or methyl;

R⁴ is optionally substituted hydrocarbyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by a process which comprises cyclisation of appropriate β substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable copper or nickel salt followed by chlorination and then amination/amidation; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

5. A composition according to any one of the preceding claims wherein M is Cu.

6. A composition according to any one of the preceding claims wherein x has a value of 0.5 to 3.5, y has a value of 0.5 to 3.5 and z has a value of 0.5 to 3.5.

7. A composition according to any one of the preceding claims wherein R¹, R² and R³ are independently H or methyl and R⁴ is optionally substituted aryl.
8. A composition according to any one of the preceding claims wherein R⁴ is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents.
9. A composition according to any one of the preceding claims wherein R⁴ is phenyl bearing a single sulfo substituent.
10. A composition according to any one of claims 1 to 6 wherein R¹ and R² independently are H or methyl and R³ and R⁴ together with the nitrogen atom to which they are attached represent an optionally substituted 3 to 8 membered aliphatic or aromatic ring.
11. A composition according to any one of claims 1 to 6 wherein R¹ and R² independently are H or methyl, R³ is H or optionally substituted C₁₋₈alkyl and R⁴ is optionally substituted C₁₋₆alkyl.
12. A composition according to claim 11 wherein R¹ and R² are H, R³ is H or C₁₋₄alkyl bearing at least one acid substituent selected from the group consisting of -SO₃H, -COOH or -PO₃H₂ and R⁴ is C₁₋₄alkyl bearing at least one acid substituent selected from the group consisting of -SO₃H, -COOH or -PO₃H₂.
13. A composition according to any one of claims 1 to 11 wherein R¹ and R² are H.
14. A composition according to claim 11 or claim 12 wherein R¹, R² and R³ are H, R⁴ is -CH₂CH₂SO₃H and y is less than 1.
15. A composition according to claim 11 wherein R¹ is H, R² is CH₃, R³ is H and R⁴ is -CH₂CH₂SO₃H.
16. A composition according to claim 11 wherein R¹ and R² are CH₃, R³ is H and R⁴ is -CH₂CH₂SO₃H.
17. A composition according to any one of the preceding claims wherein at least 70% by weight of the total amount of phthalocyanine dye is of Formula (1).
18. A composition according to claim 17 wherein at least 90% by weight of the total amount of phthalocyanine dye is of Formula (1).
19. A composition according to any one of the preceding claims wherein the dyes of Formula(1) are free from fibre reactive groups.

20. A composition according to any one of the preceding claims which comprises:

- (a) from 0.1 to 20 parts of compounds of Formula (1); and
- (b) from 80 to 99.9 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

21. A composition according to claim 20 which comprises:

- (a) from 0.5 to 15 parts of compounds of Formula (1); and
- (b) from 85 to 99.5 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

22. A composition according to claim 20 which comprises:

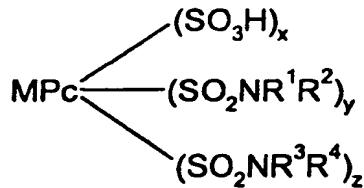
- (a) from 1 to 5 parts of compounds of Formula (1); and
- (b) from 95 to 99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

23. A composition according to any one of the preceding claims wherein the liquid media may contain additional components conventionally used in ink-jet printing inks.

24. A composition according to any one of the preceding claims which is an ink suitable for use in an ink-jet printer.

25. A mixture of dyes of Formula (4) and salts thereof:

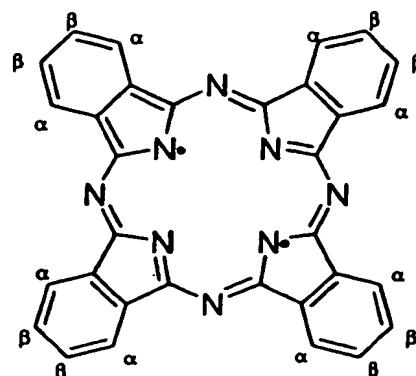


Formula (4)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



R^1 and R^2 independently are H or optionally substituted C_{1-4} alkyl;

R^3 is H or optionally substituted C_{1-6} alkyl;

R^4 is optionally substituted C_{1-6} alkyl or phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents other than amino or substituted amino; or

R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring;

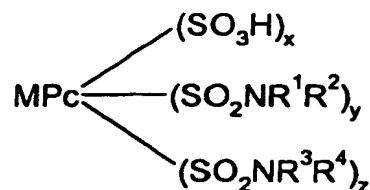
x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of $(x+y+z)$ is 4; and the substituents, represented by x , y and z , are attached only to a β -position on the phthalocyanine ring.

26. A mixture of dyes according to claim 25 of Formula (4) and salts thereof:

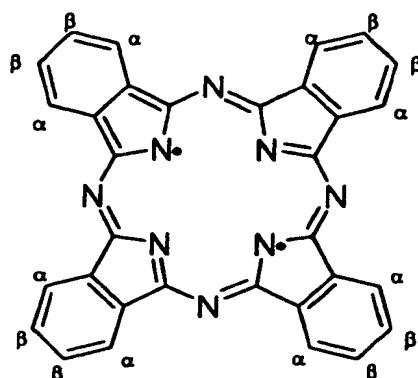


Formula (4)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula;



R^1 and R^2 independently are H or optionally substituted C_{1-4} alkyl;

R^3 is H or optionally substituted C_{1-8} alkyl;

R^4 is optionally substituted C_{1-8} alkyl or phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents other than amino or substituted amino; or

R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring;

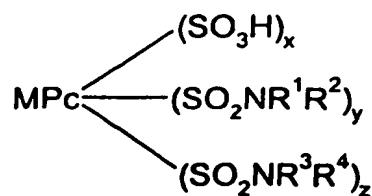
x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and the substituents, represented by x, y and z, are attached only to a β -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are prepared by a process which comprises cyclisation of appropriate β -sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base followed by chlorination and then amination/amidation.

27. A mixture of dyes according to either claim 25 or claim 26 of Formula (2) and salts thereof:

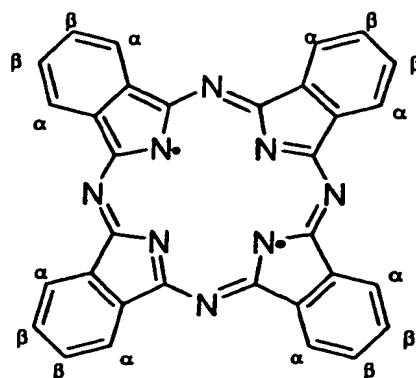


Formula (2)

wherein:

M is Cu;

Pc represents a phthalocyanine nucleus of formula;



R^1 , R^2 and R^3 independently are H or methyl;

R^4 is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents other than amino or substituted amino;

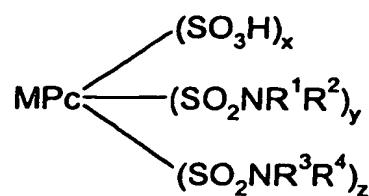
x is 0.5 to 3.5;

y is 0.5 to 3.5;

z is 0.5 to 3.5;

the sum of $(x+y+z)$ is 4; and the substituents, represented by x , y and z , are attached only to a β -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are prepared by a process which comprises cyclisation of appropriate β -sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base followed by chlorination and then amination/amidation.

28. A mixture of dyes according to either claim 25 or claim 26 of Formula (3) and salts thereof:

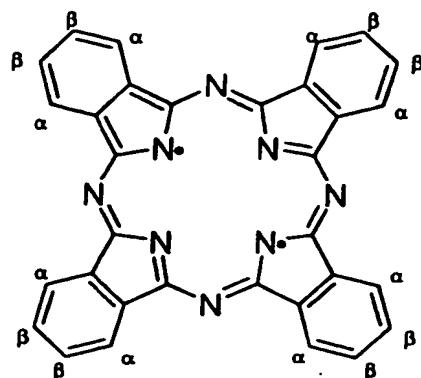


Formula (3)

wherein:

M is Cu;

Pc represents a phthalocyanine nucleus of formula;



R^1 and R^2 independently are H or methyl;

R^3 and R^4 independently are C₁₋₄alkyl bearing at least one acid substituent, selected from the group consisting of -SO₃H, -COOH or -PO₃H₂;

x is 0.5 to 3.5;

y is 0.5 to 3.5;

z is 0.5 to 3.5;

the sum of (x+y+z) is 4; and the substituents, represented by x, y and z, are attached only to a β -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are prepared by a process which comprises cyclisation of appropriate β -sulfo substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base followed by chlorination and then amination/amidation.

29 A mixture of dyes according to any one of claims 25 to 28 wherein R^1 and R^2 are H.

30. A mixture of dyes according to either claim 25 or claim 26 wherein R^1 , R^2 and R^3 are H, R^4 is -CH₂CH₂SO₃H and y is less than 1.

31. A mixture of dyes according to either claim 25 or claim 26 wherein R^1 is H, R^2 is CH₃, R^3 is H and R^4 is -CH₂CH₂SO₃H.

32. A mixture of dyes according to either claim 25 or claim 26 wherein R^1 and R^2 are CH₃, R^3 is H and R^4 is -CH₂CH₂SO₃H.

33. A mixture of dyes according to either claim 25 or claim 26 wherein R^1 and R^2 independently are H or methyl and R^3 and R^4 together with the nitrogen atom to which they are attached represent an optionally substituted 3 to 8 membered aliphatic or aromatic ring.

34. A mixture of dyes according to any one of claims 25 to 33 free from fibre reactive groups.

35. A composition which comprises a major dye component which is a mixture of phthalocyanine dyes of Formula (4), as defined in any one of claims 25 to 34, and water.
36. A composition according to claim 35 which is an ink suitable for use in an ink-jet printer.
37. A process for forming an image on a substrate comprising applying a composition according to claim 24 or claim 36 thereto by means of an ink-jet printer.
38. A material printed with a composition according to any one of claims 1 to 24, 35 or 36 or a dye according to any one of claims 25 to 34.
39. A material according to claim 38 which is a photograph printed using a process according to claim 37.
40. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is according to claim 24 or claim 36.